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Heats of formation of Zirconium binary transition metal alloys

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Abstract

D-band model is used to predict enthalpies of formation of binary transition metal alloys. One of the input parameters of the model namely bandwidth is optimized by refinement procedures based on ab initio calculations and reliable calometric data for Zr-, Hf- and Ti-compounds. Revised values of enthalpies of formation ΔH^{for} for Zr-binary transition metal compounds using new values of bandwidth $W_{Zr}^{*} = 7.24\,eV$ are substantially improved. This improvement can be applied for other problematic cases in order to ameliorate results of ΔH^{for} calculated by d-band model.

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Keywords: enthalpy of formation, binary trasition metal compounds, d-band model.

1. Introduction:

Predictions of heats of formation of alloys, ΔH, have been the object of considerable recent attention. Its experimental and theoretical determination is therefore of particular interest for technological applications. Bennett – Watson's model (means d- band's model) [1] is an important approach used to predict enthalpies of formation of binary transition metal compounds at equiatomic composition. In first step of present work we have compared recent experimental results with d-band predictions [2] for intermetallic compounds TM (T=Ti, Zr, Hf and M= Co, Ni, Ir, Ru, Rh, Pt, Pd). The raison of this choice of compounds is due to available experimental and ab initio calculations data for their enthalpies of formation.

Figure (1) reveals the general problem for some Zr-based compounds that original values of enthalpies of formation ΔH_d^0 are far from experimental data $\Delta H_{\exp}$ and ab initio calculations ΔH_{DFT} (table 1), in contrast with values of ΔH_d^0 for Hafnium and Titanium based compounds, where relatives errors are 23% for Ti-based compounds and 18% for Hf-based compounds, relative error for Zr-based compounds is close to 28%. We conclude that d-band model is very unsatisfactory for Zr-based compounds (Fig. 1) for witch the present work suggests a substantial improvement. We focused our attention on the original parameters of the original model, and on their values derived and applied by Bennett and Watson 28 years ago.

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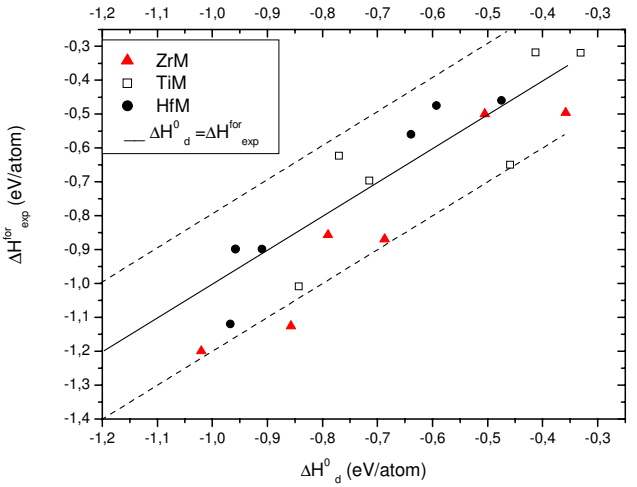

Fig (1): Experimental values of enthalpies of formation for compounds TM (T= Zr, Hf, Ti; M= Co, Ni, Ir, Ru, Rh, Pt, Pd)[8,9,10]compared with original values of d-band model[2].Dashed lines present acceptance error defined by $\pm 0.21(\mathrm{eV/atm})$

2. Calculations of bandwidths W^* and revised values of heats of formation:

The enthalpy of formation of equiatomic AB compounds is estimated from Bennett-Watson model [1, 2] according to:

$$\Delta H_d = N_{AB}.C_{AB} - \frac{N_{AB}.(10-N_{AB}).W_{AB}}{20} - \frac{1}{2}\left\{N_A C_A + N_B C_B - \frac{N_A(10-N_A)}{20}.W_A - \frac{N_B.(10-N_B)}{20}.W_B\right\} \quad N_A, N_B$$

and $N_{AB} = \frac{N_A + N_B}{2}$ number of occupied d level in metals A , B and the alloy, respectively,

and $C_{AB} = \frac{C_A + C_B}{2}$ (2)

$$W_{AB} = \left[W_A.W_B + 3(C_A - C_B)^2\right]^{1/2} \quad (3)$$

with C_A, C_B, C_{AB} and W_A, W_B, W_{AB} are centers and larger of d band of metals A, B and compounds AB, respectively.

C and N parameters are well defined from d band calculations [2,3], in contrast to the parameter W related to the approximation of Friedel [4] who propose a rectangular density of states for transition metals and their binary equiatomic compounds [2,5].

Although, it is well known that such d-band parameters should be critically investigated on the basis of ab initio calculation [6]. We consist in the application of density functional theory (DFT) approach [7] by which the enthalpies of formation ΔH_{DFT} for 50-50 binary compounds [6] TM (T=ti, Zr, Hf; M= Ru, Rh, Ir, Pt) were calculated. This results were used to estimate the larger of d-band (named bandwidth) W^* (table 1) by application of equation (1) by keeping d-band parameters (density of state N and centre of d-band) fixed. Comparison between ΔH_{DFT} and original values of heat of formation of Bennett and Watson (d-band's model) ΔH_d^0 [2] show a

reasonable agreement for TiM (22.58%) and HfM(18.01) compounds. However, for ZrM compounds values of ΔH_d^0 present important difference with their ΔH_{DFT} values, average percentage is presented in table 1.

Table(1): DFT results of enthalpies of formation ΔH_{DFT} for TM compounds (T= Ti, Hf, Zr and M= Ru, Rh, Ir, Pt) and their ground state structures compared to the original results ΔH_d^0 from d-band's model and refined values W_{DFT}^* for Ti, Zr and Hf, as obtained from adjusting ΔH_d^0 to ΔH_{DFT}.

	$\Delta H_{DFT}(eV/atm)$	structure	$\Delta H_d^0(ev/atm)$	Relative errors (%)	$W_{DFT}^*(eV)$
TiRu	-0.743	B2	-0.623	16.15	7.26
TiRh	-0.726	$L1_0$	-0.696	4.13	6.88
TiIr	-0.820	$L1_0$	-1.109	35.24	7.31
TiPt	-0.896	B19	-1.208	34.82	7.37
Average				22.58	7.20
ZrRu	-0.641	B2	-0.769	19.96	7.09
ZrRh	-0.778	B33	-0.857	10.15	7.03
ZrIr	-0.822	B33	-1.126	36.98	7.45
ZrPt	-1.062	B33	-1.538	44.82	7.68
Average				27.97	7.31
HfRu	-0.871	B2	-0.898	3.09	7.71
HfRh	-0.927	B33	-0.898	3.12	7.92
HfIr	-0.988	B33	-1.281	29.65	7.50
HfPt	-1.179	B33	-1.606	36.21	7.97
Average				18.01	7.77

Results of W_{DFT}^* are compared with W_d^0 ; original values of Bennett-Watson[2] in table (3).

As a second step, we have retrieved bandwidth's values $W_{\exp}^*$ from adjusting ΔH_d^0 to experimental data $\Delta H_{\exp}$ for TM compounds (T= Ti, Hf, Zr and M= Co, Ni, Ru, Rh, Ir) as shown in table (2).

$W_{\exp}^*$ are also compared with W_d^0 and W_{DFT}^* table (3). We conclude that the change of W_{Zr}^* is considerably having in mind the original values of $W_d^0 = 7.35eV$. In contrast to that for Hf and Ti were the difference is very small between W_{DFT}^* and original values W_d^0 as listed in table (3). Original values of enthalpies of formation ΔH_d^0 are also presented.

Table (2): revised bandwidth values W^{*}_{exp} for Ti-, Zr- and Hf- based binary 50/50 compounds obtained by adjusting d-band's model to experimental data ΔH_{exp}.

	$\Delta H_{exp}(eV/atm)$	$W^{*}_{exp}(eV)$
TiCo	-0.413 [8]	7.09
TiCo	-0.443 [9]	7.11
TiNi	-0.331 [8]	7.34
TiNi	-0.340 [9]	7.38
TiNi	-0.339 [8]	7.46
TiRu	-0.770 [8]	7.31
TiRh	-0.715 [8]	7.29
TiRh	-0.744 [8]	7.41
TiRh	-0.750 [9]	7.44
TiIr	-0.843 [8]	6.75
TiIr	-0.840 [8]	6.89
Average		7.22
ZrCo	-0.358 [8]	7.25
ZrCo	-0.422 [9]	7.29
ZrNi	-0.505 [8]	7.20
ZrNi	-0.565 [10]	7.21
ZrRu	-0.687 [8]	7.31
ZrRh	-0.790 [8]	7.26
ZrRh	-0.758 [9]	7.22
ZrRh	-0.759 [8]	7.22
ZrIr	-0.857 [8]	7.18
ZrIr	-0.810 [9]	7.12
Average		7.22
HfCo	-0.475 [8]	7.69
HfCo	-0.428 [8]	7.63
HfCo	-0.510 [9]	7.57
HfNi	-0.593 [8]	7.69
HfNi	-0.483 [8]	7.76
HfNi	-0.479 [9]	7.80
HfRu	-0.918 [8]	7.59
HhRh	-0.958 [8]	7.91
HfRh	-0.820 [9]	7.90
HfIr	-0.967 [8]	7.48
HfIr	-0.977 [9]	7.71
Average		7.70

Table (3): refined bandwidth values derived from the two refining procedures (see table 1 and 2).

	Ti	Zr	Hf
$W_d^0\ (eV)$	7.19	7.35	7.80
$W^{*}_{DFT}\ (eV)$	7.20	7.31	7.77
$W^{*}_{exp}(eV)$	7.22	7.07	7.70
average	7.20	7.24	7.75

Table (4): Results of enthalpies of formation derived by applying d-band's model with revised parameter of bandwidth for Zr $W^{*}_{Zr} = 7.24\text{eV}$ compared with experimental data and original values of heats of formation.

	$\Delta H_{\exp}(eV/atm)$	$\Delta H^{0}_{d}(ev/atom)$	$\Delta H^{rev}_{d}(ev/atom)$
ZrCo	-0.358	-0.496	-0.456
ZrCo	-0.422		
ZrNi	-0.505	-0.500	-0.521
ZrNi	-0.565		
ZrRu	-0.687	-0.769	-0.650
ZrRh	-0.790	-0.857	-0.758
ZrRh	-0.758		
ZrRh	-0.759		
ZrIr	-0.857	-1.126	-0.950
ZrIr	-0.810		
ZrPt	-1.10	-1.538	-1.25
ZrFe	-0.349	-0.288	-0.301
ZrPd	-0.640	-1.053	-0.890

Table 4 summarize our results of optimized bandwidth retining from ab initio calculations and experimental data of heats of formation and their average values compared as original values of d-band calculations of Bennett-Watson's model[2]. Average values of $W^{*}_{av}(eV)$ for Ti and Hf are in good agreement with original ones; whereas for Zr W^{*}_{av} is much larger then W^{0}_{d}.

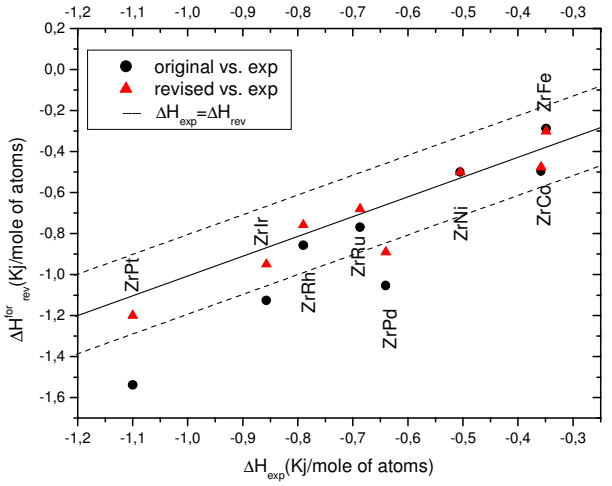

Fig (2): Experimental values of enthalpies of formation for Zr -compounds 50/50 [8,9,10] are compared to d-band model's values[2,3] (black circles) and revised values (up red triangles) using new bandwidth for Zr ; $W^{*}_{Zr} = 7.24\text{eV}$. Error acceptance (dashed lines) defined by $\Delta H_{\exp} \pm 0.1(\text{eV/atm})$

3. Conclusion:

Revised values of enthalpies of formation of binary compounds TM (T= Ti, Hf, Zr and M= Co, Ni, Ru, Rh, Ir, Pd, Pt) of d-band's model by application of equation (1); designing by ΔH_d^{rev} by injecting new values of bandwidth, $W_{Zr}^{*} = 7.24eV$ are compared with experimental data for Zr-based 50/50 compounds as shown in figure(2).

This comparison shows that revised values of enthalpies of formation ΔH_d^{rev} are considerably improved. It can be seen that only one case keeps far from experimental data ZrPd.

We conclude that in the present work we have optimized values of bandwidth witch are used to refined d-band's values of enthalpies of formation ΔH^{for} to experimental data. We note that the same procedures were used by Chen et al [6] to refined Miedema's values of ΔH^{for} for transition metal based alloys and they found also that Zr-compounds present a special case.

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